

UDC 666.172.3/5:666.031.14

EFFECT OF SMALL AMOUNTS OF SODIUM MOLYBDATE ON THE OPTICAL CHARACTERISTICS OF HOUSEHOLD GLASS

I. A. Bulycheva,¹ V. P. Krokhin,¹ and A. P. Khodykin¹Translated from *Steklo i Keramika*, No. 2, pp. 12–13, February, 1998.

It is shown that the introduction of sodium molybdate for decolorizing household glass has a positive effect on its optical properties. The additive is recommended for use in glass plants.

The causes of the appearance of an undesirable yellowish-green tint in household glass and recommendations on its elimination were described in [1]. Today the problem of glass decoloration still remains important.

Plants producing household glass use various methods of physical and chemical decoloration. However, in accordance with the data in [2], glasses containing arsenic and cerium oxide acquire a yellowish-green color when solarized.

In order to protect the environment, arsenic has to be replaced by nontoxic compounds, taking into account that nickel decoloration can be used only for glasses with a potassium composition and the main drawback of metallic selenium is its sensitivity to the oxidizing-reducing conditions of the glass melting process.

The Belgorod State Engineering Academy of Building Materials (BelSEABM) studied the possibility of using sodium molybdate instead of cobalt and metallic selenium for decoloration and improving the tint of colorless sodium-calcium-silicate glass for household purposes (Application 93046759/33 for RF patent).

There are no published data on introduction of sodium molybdate in the composition of household glass. There are data that sodium molybdate has been used in the composition of phosphate glasses and enamel coatings in order to increase the brightness of the color (USSR Inv. Certif. 1502501) [3].

In accordance with the data in [4] the melting temperature of sodium molybdate lies within 700–900°C, in accordance with [5], it is even lower (687°C). Sodium molybdate decomposes by the reaction [6]



In order to determine the effect of sodium molybdate on the illumination engineering and colorimetric characteristics of household glass, we conducted several experiments on

melting of sodium-calcium-silicate glass from the Popasnyansky glass plant. The composition of the glass included (here and below in mass fractions) $72.8 \pm 0.5\%$ SiO_2 , $0.6 \pm 0.3\%$ Al_2O_3 , $5.8 \pm 0.3\%$ CaO , $3.8 \pm 0.3\%$ MgO , $15.15 \pm 0.3\%$ Na_2O , $1.5 \pm 0.3\%$ K_2O , $0.4 \pm 0.01\%$ SO_3 .

Three variants of soda batches with 0.003, 0.006, 0.012 and 0.060% (in excess of 100%) sodium molybdate additives of analytically pure grade (99.5% basic substance) plus one variant without any additives were prepared. In addition, quartz sand was introduced in the first three compositions except for the fractions 0.1 mm and finer than 0.1 mm in size; the fourth composition did contain these fractions.

The tested glasses were melted in a laboratory electric furnace with silit heaters at $1470 \pm 10^\circ\text{C}$. The melt was poured into metallic molds onto a metallic substrate and annealed in a muffle furnace at $550 \pm 10^\circ\text{C}$.

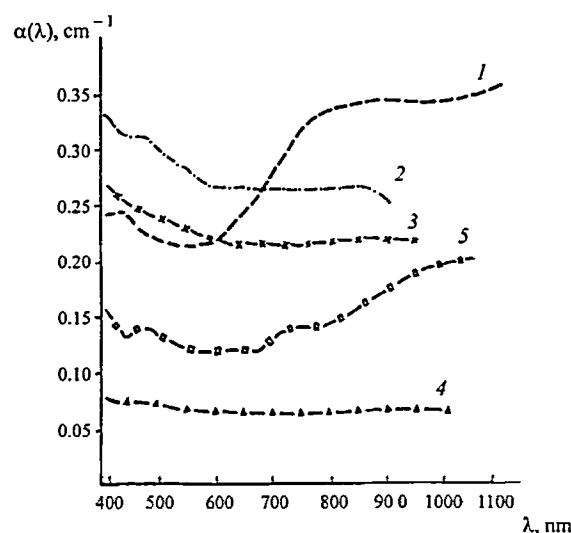


Fig. 1. Absorption curves of various glasses: 1) with no additive; 2, 3, 4, and 5) glasses with 0.003, 0.006, 0.0012 and 0.060% MoO_3 respectively; integral attenuation parameter of the glass (cm^{-1}) is 1) 0.3949; 2) 0.1530; 3) 0.1259; 4) 0.0740; 5) 0.1080.

¹ Belgorod State Engineering Academy of Building Materials, Belgorod, Russia.

A visual examination of the experimental samples showed that they were transparent and contained no traces of incomplete melting. Polished specimens 2 and 10 mm thick were fabricated from these species; their integral light transmission was measured using an IF-16 device, the spectral aperture transmission was determined using a SF-4 device in the 360 – 1100 nm wavelength range, and the colorimetric characteristics were determined using the "Color" program.

The data obtained were compared by the spectrophotometric method in [7] based on the assumption that the light absorption spectrum of the specimens consisted of the light absorption spectra of the constituent coloring components. Therefore the figure presents the spectral characteristics in the form of the curves of the absorption parameters determined by the equation

$$\alpha(\lambda) = -\lg \tau(\lambda) - D\rho(\lambda)/l,$$

where $\tau(\lambda)$ is the transmissivity, rel. units; $D\rho(\lambda)$ is a correction allowing for reflection; and l is the thickness of the specimen, rather than in the form of transmission curves.

It can be seen that the spectra of the absorption parameters of glasses containing sodium molybdate change substantially relative to the spectra of the glass containing no additive. The curves behave symbatically relative to each other. This is explainable by the fact that the melting technology used provides that the ratio of iron oxide to molybdenum in the studied glasses is the same. The higher the integral attenuation factor of the glass, the higher the curve lies.

Judging by the maximum on curve 1 at a wavelength of 1000 nm, the content of Fe(II) is high. With the introduction of sodium molybdate into compositions 2 and 3, the absorption maximum shifts to the short-wave and visible regions. This makes it possible to assume that the additives have a favorable effect on the shift of $\text{Fe(II)} \rightleftharpoons \text{Fe(III)}$ equilibrium toward trivalent iron. The behavior of curve 4 indicates complete decoloration of the glass.

Some optical and colorimetric properties of the glasses are presented in the table.

We established that the hue in glasses containing 0.003 – 0.060% sodium molybdate (as recalculated for MoO_3) shifts from 572 nm (initial glass) to 484 nm. The color intensity in the glasses decreases from 5 to 3%.

However, it should be noted that when the additive is introduced in the amount of 0.060% (as recalculated for MoO_3), the hue and the intensity stop shifting. It seems that the presence of a large amount of dust fractions of quartz sand containing a large amount of iron impurities weakens the action of the additive.

TABLE 1

Composition	Content of MoO_3 , %	Refractive index	Integral light transmission, %	Chromaticity coordinates		Hue, nm	Intensity, %
				X	Y		
1	Without additive	1.499	87.7	0.3177	0.3273	572	5
2	0.003	1.527	87.7	0.3101	0.3181	487	3
3	0.006	1.527	89.3	0.3107	0.3188	484	3
4	0.012	1.533	94.3	0.3110	0.3193	485	3
5	0.060	1.533	90.3	0.3103	0.3185	484	3

It follows from the analysis of the colorimetric properties that the light absorption caused by iron oxides can be decreased by introducing sodium molybdate, which shifts the hue to the region of purple and violet. The latter are additive with respect to the yellow-green color. It is sufficient to introduce 0.06 – 0.012% molybdenum oxide in order to neutralize the yellow-green color.

The introduction of 0.003 – 0.060% additive gives virtually the same results. Since sodium molybdate is an expensive component, it is recommended that 0.006 – 0.012% additive introduced in a preliminary concentrated batch be used. It is also expedient to remove dust fractions 0.1 and less than 0.1 mm in size from the quartz sand.

On the whole, the curves of the spectral aperture transmissivity of the initial glass differ from those of specimens containing sodium molybdate, although the hue and intensity of the color of the specimens with additives remain approximately the same.

Thus, the use of sodium molybdate for decoloration household glass allowed us to obtain glasses with higher light transmission no worse than that obtained with arsenic oxide. The use of the suggested method makes it possible to eliminate the use of arsenic in the manufacturing process, which will improve the sanitary and hygienic conditions of production.

REFERENCES

1. I. A. Bulycheva and V. P. Krokhin, "Improving the quality of household glass," *Steklo Keram.*, No. 11 – 12, 8 – 10 (1994).
2. I. Kotsik, I. Nebrzhenskii, and I. Fanderlik, *Glass Coloring* [Russian translation], Stroiizdat, Moscow (1983).
3. G. A. Makhlina, "An investigation of the absorption spectra of molybdenum and tungsten ions in phosphate glasses," *Author's Abstract of Candidate's Thesis* [in Russian], GOI (1967).
4. *Encyclopedic Chemical Dictionary* [in Russian], Sov. Entsiklopediya, Moscow (1983).
5. *Properties of Elements, A Reference Book* [in Russian], Metallurgiya, Moscow (1985).
6. *A Reference Book on Thermodynamic Quantities* [in Russian], Promizdat, Moscow (1971).
7. T. I. Veinberg, "Light absorption and spectrophotometric analysis of optical glasses," *Opt. Mekh. Zh.*, No. 2, 38 – 43 (1973).